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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference A3/0723 PK/rs	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/SG2003/000252	International filing date (day/month/year) 23 October 2003	Priority date (day/month/year) 25 October 2002
International Patent Classification (IPC) or national classification and IPC Int. Cl. <sup>7</sup> C08G 61/10; H05B 33/14		
Applicant AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.	
2. This REPORT consists of a total of 3 sheets, including this cover sheet.	
3. This report is also accompanied by ANNEXES, comprising:	
a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of 15 sheets, as follows:	
<input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).	
<input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.	
b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or table related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).	
4. This report contains indications relating to the following items:	
<input checked="" type="checkbox"/> Box No. I	Basis of the report
<input type="checkbox"/> Box No. II	Priority
<input type="checkbox"/> Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
<input type="checkbox"/> Box No. IV	Lack of unity of invention
<input checked="" type="checkbox"/> Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
<input type="checkbox"/> Box No. VI	Certain documents cited
<input type="checkbox"/> Box No. VII	Certain defects in the international application
<input type="checkbox"/> Box No. VIII	Certain observations on the international application

Date of submission of the demand 4 February 2004	Date of completion of the report 31 January 2005
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustrialia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer DR. A TESSEMA Telephone No. (02) 6283 2271

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/SG2003/000252

## Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1 (b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the elements of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):
- ☐ the international application as originally filed/furnished
- ☒ the description:
- pages 1, 2, 5-18 as originally filed/furnished
  - pages\* 3-4a received by this Authority on 12 January 2005 with the letter of 12 January 2005
  - pages\* received by this Authority on with the letter of
- ☒ the claims:
- pages as originally filed/furnished
  - pages\* as amended (together with any statement) under Article 19
  - pages\* 19-25e received by this Authority on 12 January 2005 with the letter of 12 January 2005
  - pages\* received by this Authority on with the letter of
- ☐ the drawings:
- pages as originally filed/furnished
  - pages\* received by this Authority on with the letter of
  - pages\* received by this Authority on with the letter of
- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to the sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to the sequence listing (*specify*):

\* If item 4 applies, some or all of those sheets may be marked "superseded."

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/SG2003/000252

**Box No. V** Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. Statement

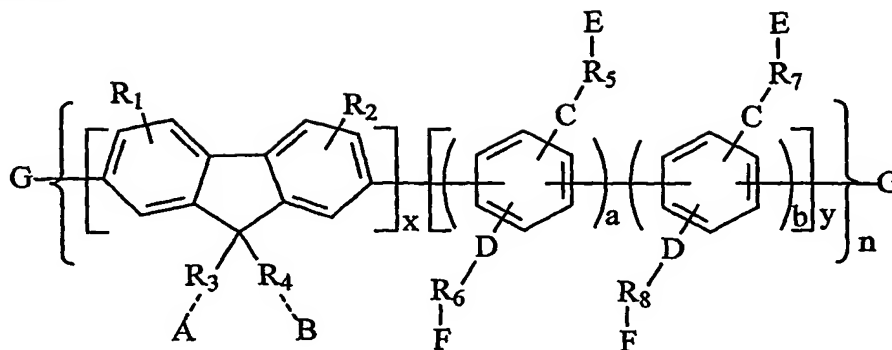
Novelty (N)	Claims 1-59	YES
	Claims	NO
Inventive step (IS)	Claims 1-59	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-59	YES
	Claims	NO

## 2. Citations and explanations (Rule 70.7)

NOVELTY; INVENTIVE STEP: Claims 1-59

No document or obvious combination of documents cited in the search report disclose a conjugate polymer having the structure defined in amended claim 1; a method of producing such a polymer or increasing the solubility, in polar solvents, of such a polymer as defined in any one of amended independent claims 22, 32, 43 and 47 has also not been disclosed by any one or obvious combination of documents cited in the search report. Therefore, present claims 1-59 are considered to satisfy the PCT requirements of novelty and inventive step.

Formula 1



wherein:

$R_1$  and  $R_2$  are identical or different and are each H, a straight or branched alkyl, alkoxy, ester groups or cyclic crown ether groups having from 1 to about 22 carbon atoms. Preferably,  $R_1$  and  $R_2$  are H or straight or branched alkyl groups having 1 to about 12 carbon atoms. More preferably,  $R_1$  and  $R_2$  are alkoxy groups with 1 to about 12 carbon atoms.

A, B, E and F (as the terminal groups), are identical or different and are each H, SiR'R'' or NR'R'' (wherein at least one of A, B, E or F is NR'R'') for the precursor polymers. Consequently, the precursor neutral polymers will contain one or more NR'R'' groups as the functional groups. These terminal groups are designed to introduce water solubility.

These polymers may be directly synthesized using monomers containing amino groups, or some of other functional groups such as Br or I which will react with amine to form the amino groups. R' and R'' are independently selected from the group consisting of hydrogen, unbranched or branched alkyl or alkoxy groups having 1 to about 12 carbon atoms, (C3 to C10) cycloalkyl groups. It is preferred that R' and R'' are C1 to C4 alkyl or alkoxy groups. Preferably, A, B, E and F are independently selected from hydrogen or NR'R'' (but not all hydrogen), where R' and R'' are as defined above.

C and D are identical or different and are each H (but can not be both H), O, S, CO, COO, CRR', NR', SiR'R'', wherein R' and R'' are as defined above.

$R_3$  and  $R_4$  are identical or different and are independently selected from linear, branched, or cyclical saturated or unsaturated aliphatic moieties which may contain one or more heteroatoms.  $R_3$  and  $R_4$  are preferably C4-C8 linear or branched aliphatic chains which may contain one or more heteroatoms. Preferably,  $R_3$  and  $R_4$  are C2-C12 alkoxy groups.

$R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are identical or different and are independently selected from linear or branched or cyclical saturated or unsaturated aliphatic moieties which may

contain one or more heteroatoms and which may contain one or more aromatic groups, substituted or unsubstituted aromatic moieties.  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are preferably C1 to C8 linear or branched aliphatic chains which may contain one or more heteroatoms, and more preferably,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are C2-C12 alkoxyl groups.

5 G is typically selected from those reactive groups that are capable of undergoing chain extension. Preferably, G is hydrogen, halogen, boronic acid, boronate radical or an aryl moiety. The aryl moiety may contain halogen, boronic acid, or boronate radical. Preferably, G is hydrogen or an unsubstituted or substituted aryl moiety which does not contain the above mentioned groups.

10 x and y are independent and each is a number from 1 to about 100 and preferably 1 to about 20 and more preferably from 1 to about 10. a and b are also independent and each is a number from 0 to about 100, wherein if a is 0, b is a number from 1 to about 100, and if b is 0, a is a number from 1 to about 100. Preferably, a and b are numbers up to 10. n will range from 1 to about 1000 and preferably from 1 to  
15 about 50.

The attachment of  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  either on the fluorene ring or on the phenylene ring, enables good solubility of the neutral polymer, which facilitates the post-polymerization approach in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). Preferably,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are alkoxyl groups with 2 to about 10 carbon  
20 atoms, since longer aliphatic chains may reduce the water-solubility of the resulting polymers. Preferably, the attachment of C and D are on the 2 and 5 positions and the linkage between fluorene and phenylene is on the 1 and 4 positions.

In one embodiment having liquid crystalline properties, the fluorene portion of Formula 1 is 9,9-dihexylfluorene, C and D are oxygen atoms, and  $R_6$  and  $R_7$  are C2 to  
25 C12 alkyl groups, and the terminal groups E and F are ethyl amino groups. The corresponding water-soluble polymers have also shown liquid crystalline properties.

The polymers may either be homopolymers or copolymers (such as random copolymers or alternated copolymers).

According to a second aspect of the invention, there is provided a method of  
30 increasing the solubility, in polar solvents, of the polymers described above by quaternizing terminal amino groups of the polymer. Typically the quaternization is effected by treating the polymer with an alkyl bromide, such as bromoethane. In one embodiment of this method, the polymer may be treated with bromoethane by stirring the polymer with the bromoethane in dimethyl sulfoxide (DMSO) and tetrahydrofuran

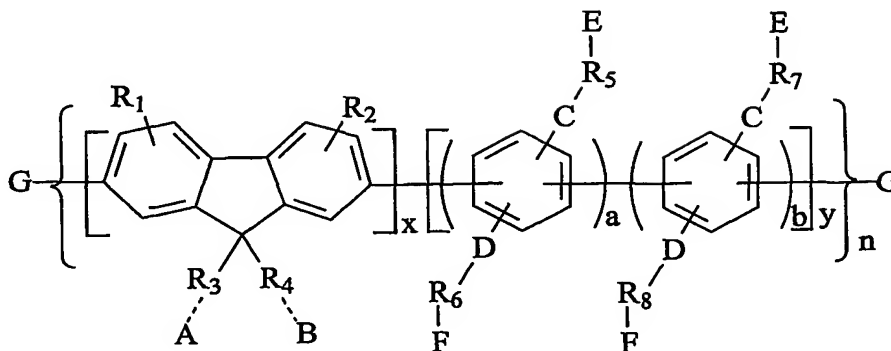
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(THF). The mix of DMSO and THF solvents may be in a ratio of 1:4 and the stirring may be effected at a temperature of about 50°C for about 5 days. In another embodiment of this method, the polymer may simply be treated with bromoethane by stirring the polymer with bromoethane in THF solvent. In this case, the stirring may be effected at about room temperature for about 24 hours. The above two embodiments result in different quarterization degrees of the polymer.

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Claims

The claims defining this invention are as follows:

- 5 1. Conjugated polymers of the formula:



wherein:

- $R_1$  and  $R_2$  are identical or different and are each H, a straight or branched alkyl, alkoxy, ester groups or cyclic crown ether groups having from 1 to about 22 carbon atoms;
- A, B, E and F are identical or different and are each H, Si R'R'' or NR'R'' (but can not all be H or SiR'R''); R', and R'' are independently selected from the group consisting of hydrogen, unbranched or branched alkyl or alkoxy groups having 1 to about 12 carbon atoms, (C3 to C10) cycloalkyl groups;
- C and D are identical or different and are each H (but can not both be H), O, S, CO, COO, CRR', NR', Si R'R'', wherein R' and R'' are as defined above;
- $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are identical or different and are independently selected from linear or branched or cyclical saturated or unsaturated aliphatic moieties which may contain one or more heteroatoms and which may contain one or more aromatic groups, substituted or unsubstituted aromatic moieties;
- G is hydrogen, halogen, boronic acid, boronate radical or an aryl moiety;
- a and b are independent and each is a number from 0 to about 100;
- x and y are also independent and each is a number from 0 to about 100; and
- n is a number from 1 to about 1000.

A polymer according to claim 1, wherein the polymers are homopolymers.

3. A polymer according to claim 1, wherein the polymers are random copolymers.

5 4. A polymer according to claim 1, wherein the polymers are alternated copolymers.

5. A polymer according to any one of the claims 1 to 4, wherein  $R_1$  and  $R_2$  are H or straight or branched alkyl groups having from 1 to about 12 carbon atoms.

10

6. A polymer according to any one of claims 1 to 4, wherein  $R_1$  and  $R_2$  are alkoxy groups with from 1 to about 12 carbon atoms.

15

7. A polymer according to any one of claims 1 to 4, where  $R'$  and  $R'$  are alkyl or alkoxy groups having from 1 to 4 carbon atoms.

8. A polymer according to any one of claims to 4, wherein A, B, E and F are independently selected from hydrogen or  $NR'R''$  (but not all can be hydrogen).

20

9. A polymer according to any one of claims 1 to 4, wherein  $R_3$  and  $R_4$  are linear or branched aliphatic chains, having from 1 to 4 carbon atoms, containing one or more heteroatoms and/or one or more aromatic groups.

25

10. A polymer according to any one of claims 1 to 4, wherein  $R_3$  and  $R_4$  are alkoxy groups having from 2 to about 12 carbon atoms.

30

11. A polymer according to any one of claims 1 to 4, wherein  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are linear or branched aliphatic chains, having from 1 to about 8 carbon atoms, containing one or more heteroatoms.

12. A polymer according to any one of claims 1 to 4, wherein  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are alkoxy groups having from 2 to about 12 carbon atoms.

35

13. A polymer according to any one of claims 1 to 4, wherein x and y are each a number between 0 and 20.

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A polymer according to claim 13, wherein x and y are each a number between 0 and 10.

- 5 15. A polymer according to any one of claims 1 to 4, wherein a and b are each a number between 0 and 10.
16. A polymer according to any one of claims 1 to 4, wherein n is a number between 1 and about 50.
- 10 17. A polymer according to any one of claims 1 to 4, wherein G is an aryl moiety containing halogen, boronic acid or boronate radical.
- 15 18. A polymer according to any one of claims 1 to 4, wherein G is hydrogen or an unsubstituted or substituted aryl moiety which does not contain halogen, boronic acid or boronate radical.
19. A polymer according to any one of claims 1 to 4, wherein the linkage between fluorene and phenylene is on the 1 and 4 positions.
- 20 20. A polymer according to any one of claims 1 to 4, having a backbone comprising extended phenylene units.
21. A polymer according to any one of claims 1 to 4, having a backbone comprising extended fluorene units.
- 25 22. A method of increasing the solubility, in polar solvents, of the polymers of any one of claims 1 to 21 by quaternizing terminal amino groups of the polymer.
- 30 23. A method according to claim 22, wherein said quaternization is effected by treating the polymer with an alkyl bromide.
24. A method according to claim 23, wherein the alkyl bromide is bromoethane.
- 35 25. A method according to claim 24, wherein the polymer is treated with bromoethane by stirring the polymer with bromoethane in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF).

A method according to claim 25, wherein the ratio of DMSO and THF is about 1:4, and the stirring is effected at about 50°C for about 5 days.

- 5 27. A method according to claim 24, wherein the polymer is treated with bromoethane by stirring the polymer with bromoethane in tetrahydrofuran.
28. A method according to claim 27, wherein the stirring is effected at about room temperature for about 24 hours.
- 10 29. A method according to any one of claims 25 to 28, comprising the further steps of:
- evaporating the solvents;
  - precipitating the quaternized polymer;
  - washing the polymer; and
  - 15 • drying the polymer.
30. A method according to claim 29, wherein the polymer is precipitated by adding acetone followed by centrifugation.
- 20 31. A method according to claim 29 wherein the washing is effected with chloroform and/or acetone.
32. A method of forming a conjugated cationic polymer, having a desired solubility in a given solvent, said method comprising:
- 25 • providing a polymer of any one of claims 1 to 21;
- determining a desired solubility of the polymer in the given solvent;
  - quaternizing terminal amino groups of the polymer to an extent necessary to increase the solubility of the polymer to the desired solubility.
- 30 33. A method according to claim 32, wherein between about 30% and about 80% of the terminal amino groups undergo quaternization.
34. A method according to claim 32, wherein said quaternization is effected by
- 35 treating the polymer with an alkyl halide.
35. A method according to claim 34, wherein the alkyl halide is bromoethane.

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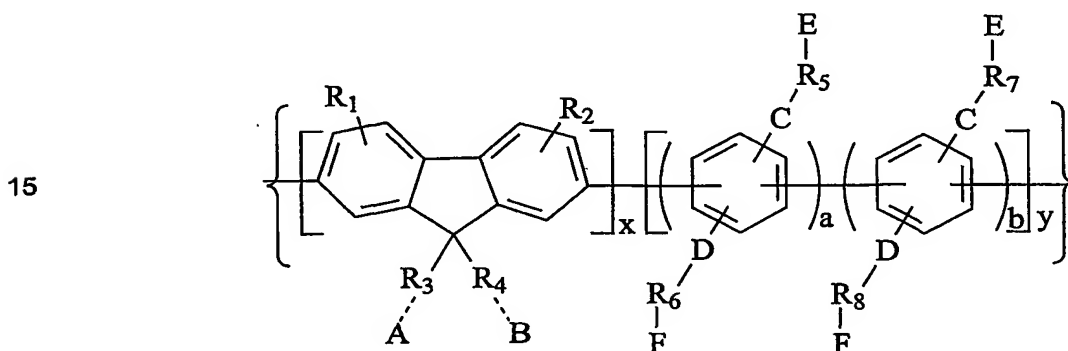
- 5
36. A method according to claim 35, wherein the polymer is treated with bromoethane by stirring the polymer with bromoethane in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF).
- 10
37. A method according to claim 36, wherein the ratio of DMSO and THF is about 1:4, and the stirring is effected at about 50°C for about 5 days.
38. A method according to claim 35, wherein the polymer is treated with bromoethane by stirring the polymer with bromoethane in tetrahydrofuran.
- 15
39. A method according to claim 38, wherein the stirring is effected at about room temperature for about 24 hours.
- 20
40. A method according to any one of claims 36 to 39, comprising the further steps of:
- evaporating the solvents;
  - precipitating the quaternized polymer;
  - washing the polymer; and
  - drying the polymer.
41. A method according to claim 40, wherein the polymer is precipitated by adding acetone followed by centrifugation.
- 25
42. A method according to claim 40, wherein the washing is effected with chloroform and/or acetone.
- 30
43. A method of forming a conjugated cationic polymer, said method comprising:
- providing monomer precursors of a polymer of any one of claims 1 to 21;
  - quaternizing terminal amino groups of the monomer precursors; and
  - synthesizing the cationic polymer from said quaternized monomer precursors.
- 35
44. A method according to claim 43, wherein said synthesis is effected by the Suzuki coupling reaction.

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A method according to claim 43, further including the steps of determining the desired solubility of the cationic polymer and calculating the amount of monomer precursors required to form a cationic polymer having the desired solubility.

46. A method according to claim 43, further including the step of determining the desired solubility of the cationic polymer, and wherein the terminal amino groups are quaternized to a degree sufficient to result in the cationic polymer having the desired solubility.

47. A conjugated cationic polymer, derived from the polymer of any one of claims 1 to 21, said cationic polymer comprising repeating units of the formula:



wherein:

- (a)  $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, C, D, a, b, x$  and  $y$  are as defined in claim 1; and
- (b) in at least one of the repeating units, at least one of  $A, B, E$  and  $F$  is  $NR'R''R'''$ , wherein  $R', R''$  and  $R'''$  are independently selected from the groups consisting of hydrogen, unbranched or branched alkyl or alkoxy groups having 1 to about 12 carbon atoms, and  $(C_3$  to  $C_{10})$  cycloalkyl groups.

48. A cationic polymer according to claim 47, wherein at least one of  $R', R''$  and  $R'''$  is hydrogen.

49. A cationic polymer according to claim 48, wherein at least one of  $A, B, E$  and  $F$  is ammonium.

50. A cationic polymer, according to claim 49, wherein the ammonium has been quaternized from at least one amino substituent of the polymer.

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A cationic polymer according to claim 49 wherein, in more than one of the repeating units, at least one of A, B, E and F is ammonium.

52. A cationic polymer according to claim 51 wherein, in more than one of the repeating units, more than one of A, B, E and F is ammonium.
53. A cationic polymer according to claim 50 wherein between about 30% and about 60% of the amino substituents in said polymer have been quaternized to ammonium.
54. A conjugated cationic polymer formed according to the method of any one of claims 43 to 46.
55. A conjugated cationic polymer substantially as hereinbefore described with reference to any one or more of the examples.
56. A salt comprising a conjugated cationic polymer according to any one of claims 47 to 55.
57. An ionic composition comprising a cationic polymer according to any one of claims 47 to 55.
58. A method of increasing the solubility, in polar solvents, of a polymer of any one of claims 1 to 21, said method being substantially as hereinbefore described with reference to any one or more of the examples.
59. A method of forming a conjugated cationic polymer, having a desired solubility in a given solvent, said method being substantially as hereinbefore described with reference to any one or more of the examples.